Amino acids:

Optimization in underivatized formula and fragment patterns in LC/ESI-MS analysis

(a) Positive ion mode (pH < 7)

\[ \text{Base} + \text{Acid} \rightarrow [\text{Sample} \ [\text{M + H}]^+] \]

(b) Negative ion mode (pH > 7)

\[ \text{Acid} + \text{Base} \rightarrow [\text{Sample} \ [\text{M - H}]]^- \]

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The principles of acid-base theory in solution chemistry for ESI-MS optimization.
(a) Protein AAs

Tyr, [M+H]+ = 182
Phe, [M+H]+ = 166
Arg, [M+H]+ = 175
His, [M+H]+ = 156
Met, [M+H]+ = 150
Leu, [M+H]+ = 132
Lys, [M+H]+ = 147
Val, [M+H]+ = 118
Glu, [M+H]+ = 148
Pro, [M+H]+ = 116
Asp, [M+H]+ = 134
Thr, [M+H]+ = 120
Hyp, [M+H]+ = 132
Ala, [M+H]+ = 90
Ser, [M+H]+ = 106
Gly, [M+H]+ = 76

Time (min)

10 20 30 40 50

(b) Non-protein AAs

Norleu, [M+H]+ = 132
Norval, [M+H]+ = 118
α-AAA, [M+H]+ = 162
Isoval, [M+H]+ = 118
α-ABA, [M+H]+ = 104
γ-ABA, [M+H]+ = 104
β-AIBA, [M+H]+ = 104
N-Et-Gly, [M+H]+ = 104
β-Ala, [M+H]+ = 90
Sar, [M+H]+ = 90

Time (min)

10 20 30 40 50

(c) Unhydrolyzed protein AAs

Gln, [M+H]+ = 147
Asn, [M+H]+ = 133

Time (min)

10 20 30 40 50
(a) Protein AAs

Gly, [M+H]^+ = 76
Chemical Formula: C₂H₅NO₂
Exact Mass: 75.03
Molecular Weight: 75.07

Ser, [M+H]^+ = 106
Chemical Formula: C₂H₇NO₃
Exact Mass: 105.04
Molecular Weight: 105.09

Ala, [M+H]^+ = 90
Chemical Formula: C₂H₅NO₂
Exact Mass: 89.05
Molecular Weight: 89.09

Thr, [M+H]^+ = 120
Chemical Formula: C₂H₇NO₂
Exact Mass: 119.06
Molecular Weight: 119.12

Asp, [M+H]^+ = 134
Chemical Formula: C₃H₇NO₄
Exact Mass: 133.04
Molecular Weight: 133.10

Pro, [M+H]^+ = 116
Chemical Formula: C₃H₇NO₂
Exact Mass: 115.06
Molecular Weight: 115.13

Glu, [M+H]^+ = 148
Chemical Formula: C₄H₉NO₃
Exact Mass: 147.05
Molecular Weight: 147.13

Val, [M+H]^+ = 118
Chemical Formula: C₅H₁₁NO₂
Exact Mass: 117.08
Molecular Weight: 117.15
Lys, [M+H]$^+$ = 147

Chemical Formula: C$_9$H$_{14}$N$_2$O$_2$
Exact Mass: 146.11
Molecular Weight: 146.19

Leu, [M+H]$^+$ = 132

Chemical Formula: C$_9$H$_{13}$NO$_2$
Exact Mass: 131.09
Molecular Weight: 131.17

Met, [M+H]$^+$ = 150

Chemical Formula: C$_8$H$_{15}$NO$_2$S
Exact Mass: 149.05
Molecular Weight: 149.21

His, [M+H]$^+$ = 156

Chemical Formula: C$_9$H$_{14}$N$_2$O$_2$
Exact Mass: 155.07
Molecular Weight: 155.15

Arg, [M+H]$^+$ = 175

Chemical Formula: C$_9$H$_{14}$N$_2$O$_2$
Exact Mass: 174.11
Molecular Weight: 174.20

Phe, [M+H]$^+$ = 166

Chemical Formula: C$_8$H$_{15}$NO$_2$
Exact Mass: 165.08
Molecular Weight: 165.19

Tyr, [M+H]$^+$ = 182

Chemical Formula: C$_8$H$_{15}$NO$_2$
Exact Mass: 181.07
Molecular Weight: 181.19

Hyp, [M+H]$^+$ = 132

Chemical Formula: C$_9$H$_{10}$N$_2$O$_2$
Exact Mass: 131.06
Molecular Weight: 131.13
(b) Non-protein AAs

Asn, [M+H]^+ = 133

Chemical Formula: C_5H_10N_2O_3
Exact Mass: 146.07
Molecular Weight: 146.14

Gln, [M+H]^+ = 147

Chemical Formula: C_5H_10N_2O_3
Exact Mass: 146.07
Molecular Weight: 146.14

Sar, [M+H]^+ = 90

Chemical Formula: C_3H_7NO_2
Exact Mass: 89.05
Molecular Weight: 89.09

β-Ala, [M+H]^+ = 90

Chemical Formula: C_4H_9NO_2
Exact Mass: 103.06
Molecular Weight: 103.12

N-Et-Gly, [M+H]^+ = 104

Chemical Formula: C_4H_9NO_2
Exact Mass: 103.06
Molecular Weight: 103.12

β-AlBA, [M+H]^+ = 104

Chemical Formula: C_4H_9NO_2
Exact Mass: 103.06
Molecular Weight: 103.12
**α-AlBA, [M+H]⁺ = 104**

Chemical Formula: C₇H₈NO₂
Exact Mass: 103.06
Molecular Weight: 103.12

**γ-ABA, [M+H]⁺ = 104**

Chemical Formula: C₇H₈NO₂
Exact Mass: 103.06
Molecular Weight: 103.12

**α-ABA, [M+H]⁺ = 104**

Chemical Formula: C₇H₈NO₂
Exact Mass: 103.06
Molecular Weight: 103.12

**Isoval, [M+H]⁺ = 118**

Chemical Formula: C₅H₁₀NO₂
Exact Mass: 117.08
Molecular Weight: 117.15

**Norval, [M+H]⁺ = 118**

Chemical Formula: C₅H₁₀NO₂
Exact Mass: 117.08
Molecular Weight: 117.15

**Norleu, [M+H]⁺ = 132**

Chemical Formula: C₆H₁₃NO₂
Exact Mass: 131.09
Molecular Weight: 131.17
(a) -COOH fragment

\[ [M + H - 46]^+ \]

(b) -NH\textsubscript{2} fragment

\[ [M + H - NH\textsubscript{3}]^+ \]

(c) -OH fragment

\[ [M + H - H\textsubscript{2}O]^+ \]
Application to LC x GC/C/IRMS method:
Liquid Chromatography x Gas Chromatography/ Combustion/ Isotope Ratio Mass Spectrometry

Takano et al., IJMS (2015)
References


